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REGULARITIES IN THE SECOND SPECTRUM OF XENON

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ABSTRACT

The ground doublet ($^2P_{1\frac{1}{2},\frac{1}{2}}$) in the spectrum of ionized xenon (Xe II) has been identified among lines observed in the Schumann region by Abbink and Dorgelo. The levels are separated by 10,540 wave numbers. This spectral term has been connected with others which combine so as to give lines in the visible Xe II spectrum, and the absolute values of the terms have been fixed by extrapolating series forming terms to their limits. The ionization potential of Xe^+ is found from these spectroscopic data to be approximately 21.1 volts. A partial list of identified terms and their combinations is given.

The neutral atoms of any of the rare gases, Ne, A, Kr, Xe, Ra, have, in the unexcited state, the configuration of a closed shell with two s and six p electrons, symbolized by s^2p^6, and, according to Hund's theory,[1] the spectral term which characterizes the normal state is a single level $^1S_0$. The simple ions of these gases are characterized by the electron group s^2p^5, giving rise to an inverted doublet term $^2P^\circ_{1\frac{1}{2},\frac{1}{2}}$ in the spectrum. This doublet term is of great importance in the structural analysis of rare gas spectra because the terms representing the excited states of the neutral atoms arise from the interaction of the series electron with the s^2p^5 group. With the exception of $^1S_0$, all of the spectral terms involved in the production of the first spectrum of a rare gas result from the addition in turn of ns, np, nd, and nf electrons to the $^2P^\circ_{1\frac{1}{2},\frac{1}{2}}$ term of the ion. These two levels are the convergence limits of all the term series thus obtained. The presence of two series limits in these spectra was first indicated by Paschen,[2] who found in his analysis of the Ne I spectrum that certain groups of terms converged to one limit while others converged to another one separated from the first by about 780 cm^{-1}. This displacement constant, A, was first interpreted by Grotrian,[3] who identified the two series limits as two different states of the neon ion. A strictly analogous state of affairs has since been found to exist in the spectra of the succeeding rare gases, A,[4] Kr,[5] and Xe.[6]

The results were collected[7] for comparison in our paper on the first spectrum of xenon and is repeated here for convenience in Table 1.

[1] Hund, Linienspectren und periodisches System der Elemente, p. 144, Springer; Berlin, 1927.
[2] Paschen, Ann. d. Phys., **60**, p. 405; 1919; **63**, p. 201; 1920.
[3] Grotrian, Zeitschr f. Physik, **8**, p. 116; 1921.
[4] Meissner, Zeitschr. f. Physik, **27**, p. 238, 1926; **39**, p. 172, 1926; **40**, p. 839, 1927.
[5] Meggers, de Bruin, and Humphreys, B. S. Jour. Research, **3** (RP89), p. 129; 1929.
[6] Meggers, de Bruin, and Humphreys, B. S. Jour. Research, **3** (RP115), p. 731; 1929.
[7] Meggers, de Bruin, and Humphreys, B. S. Jour. Research **3** (RP115), p. 731; 1929.

TABLE 1.—*Displacement constants and level separations in rare gas spectra*

	Neon	Argon	Krypton	Xenon
A=displacement constant	780. 0	1, 423. 20	5, 330±	Vide infra.
$^2P_{\frac{1}{2}}-{}^2P^\circ_{\frac{1}{2}}$	782	1, 431	5, 371	(9621)?
$1s_5-1s_3$	776. 90	1, 409. 92	5, 219. 90	9,129.24.
Centers of gravity $3p_{5\ldots10}-3p_{1\ldots4}$	788	1, 451	5, 353	Vide infra.

Two years ago a preliminary note on the lowest doublet ($^2P^\circ_{1\frac{1}{2}, \frac{1}{2}}$) of the first spark spectrum of xenon was published by two of us.[8] Extrapolating the separation of the lowest doublet of the spark spectra of the preceding rare gases an estimation of this separation in the Xe_{II} spectrum was arrived at, and examination of the data of Abbink and Dorgelo[9] in the Schumann region revealed a number of pairs of lines with wave number separations of 9,621 cm^{-1}, which was then interpreted as the fundamental doublet separation.

Shortly after this we completed our analysis of the Xe_I spectrum and obtained some additional estimates of the doublet separation which should characterize the Xe_{II} spectrum. "On account of the very large separation of $^2P^\circ_{1\frac{1}{2}, \frac{1}{2}}$ for xenon, it is impossible to find any but the first members of the non-Ritzian sequence $np_{1, 2, 3, 4}$, since the second members would give negative term values. It is therefore, not possible to determine the displacement constant A of xenon from the series limits. However, an upper limit can be found from the distance between centers of gravity of the $2p_{5\ldots10}$ and the $2p_{1\ldots4}$ groups. This upper limit has the value 10,540. The lower limit for this A is the $1s_5-1s_3$ separation which amounts to 9,129.24."[10] The doublet separation 9,621 mentioned above was regarded as being in satisfactory agreement with the two limits 9,129 and 10,540 just discussed, and this was accordingly assumed to be the correct separation of the $^2P^\circ_{1\frac{1}{2}, \frac{1}{2}}$ levels of Xe_{II}.

A little later we completed a new description of the spark spectra of xenon between the limits 2,230 and 8,716 A. The wave lengths and relative intensities of about 1,600 lines were observed and an analysis of the Xe_{II} spectrum in this interval was undertaken. No connection with the above-mentioned pairs of lines in the Schumann region could be found and it was concluded that the identification of 9,621 as the separation of the Xe_{II} ground doublet was wrong. Further search among the extreme ultra-violet lines revealed another recurring difference equal to 10,540 cm^{-1}, identical with the upper limit of the $^2P^\circ_{1\frac{1}{2}, \frac{1}{2}}$ separation as derived from the distance between the centers of gravity of p-term groups in the Xe_I spectrum. Pairs of lines with this difference in wave number were found to be separated by intervals which were repeated among lines in the visible spectrum of Xe^+ and the new difference was thus established beyond doubt as the sought for separation of the $^2P^\circ_{1\frac{1}{2}, \frac{1}{2}}$ levels of Xe^+. The same separation has recently been suggested by Kichlu [11] as the ground doublet of Xe_{II}; he gives eight pairs of lines in the extreme ultra-violet, but no

[8] Humphreys and deBruin, Sci., **68**, p. 573; 1928.
[9] Abbink and Dorgelo, Zeitschr. f. Physik, **47**, p. 221; 1928.
[10] Meggers, deBruin, and Humphreys, B. S. Jour. Research **3** (RP115), p. 737; 1929.
[11] Kichlu, Zeitschr. f. Physik., **64**, p. 697; 1930.

satisfactory data for testing these with related lines in the visible spectrum were available to him.

The systematic examination of the "constant differences" occurring in our data has led to the definite establishment of a large number of energy levels. The most probable identification of several of the terms on the basis of combination intensities and comparison with the similarly constituted spectrum of Kr^+ is suggested. The terms which may be theoretically expected are as follows:

TABLE 2.—*Electron configurations and spectral terms for* Xe_{II}

Electron configuration	Term limit[3] P terms	Term limit[1] D terms	Term limit[1] S terms
s^2p^5	$^2P^\circ$		
$s^2p^4.6s$	^2P, ^4P	^2D	^2S
$s^2p^4.6p$	$^2S^\circ$,$^2P^\circ$,$^2D^\circ$,$^4S^\circ$,$^4P^\circ$,$^4D^\circ$	$^2P^\circ$,$^2D^\circ$,$^2F^\circ$	$^2P^\circ$
$s^2p^4.5d$	^2P,^2D,^2F,^4P,^4D,^4F	^2S,^2P,^2D,^2F,^2G	^2D
$s^2p^4.6d$	^2P,^2D,^2F,^4P,^4D,^4F	^2S,^2P,^2D,^2F,^2G	^2D
$s^2p^4.7s$	^2P, ^4P	^2D	^2S

Our complete list of indentified terms is reserved for a later publication; a few of the most important ones are given in Table 3 where the electron configuration, term symbol, and absolute term value appear in successive columns. The highest term, $^2P^\circ_{1\frac{1}{2}} = 171{,}067$ is obtained as the approximate Rydberg limit of the *s*-electron series; it corresponds to an ionization potential of approximately 21.1 volts for the Xe^+ion.

Combinations of the terms in Table 3 are represented in Table 4 by wave lengths and estimated intensities (in parenthesis) of the resulting spectral lines, and by their corresponding wave numbers in vacuo. The calculated wave lengths and wave numbers of permitted combinations in the accessible region which have not been observed are shown in brackets. Among 45 such calculated lines 35 are combinations between terms of the doublet and quartet systems and such intersystem combinations are, in general, much weaker than the intrasystem ones.

In our investigation of the first spectrum of xenon [12] the data of Abbink and Dorgelo in the Schumann region were examined in the hope of classifying the lines given by these authors as arc lines. Several of these lines, however, remained unclassified and it seemed very doubtful if they could be attributed to Xe_I. Several of these lines are coincident with combinations of Xe_{II} terms and it seems logical to conclude that they are Xe_{II} lines. We have, therefore, included them in the table of term combinations.

[12] Meggers, de Bruin, and Humphreys, B. S. Jour. Research 3, (RP115), p. 753; 1929.

TABLE 3.—*Partial list of terms in the Xe_{II} spectrum*

Electron configuration	Series limit	Term symbol	Term value	Level differences
s^2p^5	^3P	$^2P^o_{1\frac{1}{2}}$	171, 067	
				10, 540
s^2p^5		$^2P^o_{0\frac{1}{2}}$	160, 527	
sp^6		$^2S_{0\frac{1}{2}}$	80, 194. 77	
$s^2p^4.6s$	^3P	$^4P_{2\frac{1}{2}}$	78, 000. 00	
				1, 995. 83
$s^2p^4.6s$		$^4P_{1\frac{1}{2}}$	76, 004. 17	
				1, 793. 78
$s^2p^4.6s$		$^4P_{0\frac{1}{2}}$	74, 210. 39	
$s^2p^4.5d$	^3P	$^4D_{3\frac{1}{2}}$	75, 630. 93	
				−41. 00
$s^2p^4.5d$		$^4D_{2\frac{1}{2}}$	75, 671. 93	
				636. 84
$s^2p^4.5d$		$^4D_{1\frac{1}{2}}$	75, 035. 09	
				−380. 82
$s^2p^4.5d$		$^4D_{0\frac{1}{2}}$	75, 415. 91	
$s^2p^4.6s$	^3P	$^2P_{1\frac{1}{2}}$	68, 269. 62	
				1, 446. 44
$s^2p^4.6s$		$^2P_{0\frac{1}{2}}$	66, 823. 18	
$s^2p^4.5d$		$X_{1\frac{1}{2}}$	67, 104. 71	
				1, 316. 40
$s^2p^4.5d$		$X_{0\frac{1}{2}}$	65, 788. 31	
$s^2p^4.6s$	^1D	$^2D_{2\frac{1}{2}}$	64, 166. 28	
				3. 68
$s^2p^4.6s$		$^2D_{1\frac{1}{2}}$	64, 162. 60	
$s^2p^4.6p$	^3P	$^4S^o_{1\frac{1}{2}}$	59, 276. 51	
$s^2p^4.6p$	^3P	$^4P^o_{2\frac{1}{2}}$	59, 109. 67	
				1, 553. 38
$s^2p^4.6p$		$^4P^o_{1\frac{1}{2}}$	57, 556. 29	
				160. 55
$s^2p^4.6p$		$^4P^o_{0\frac{1}{2}}$	57, 395. 74	
$s^2p^4.6p$	^3P	$^4D^o_{3\frac{1}{2}}$	57, 363. 42	
$s^2p^4.6p$		$^4D^o_{2\frac{1}{2}}$	(?)	
$s^2p^4.6p$		$^4D^o_{1\frac{1}{2}}$	54, 285. 52	
				3, 631. 85
$s^2p^4.6p$		$^4D^o_{0\frac{1}{2}}$	50, 653. 67	
$s^2p^4.6p$	^3P	$^2D^o_{2\frac{1}{2}}$	49, 012. 37	
				−427. 50
$s^2p^4.6p$		$^2D^o_{1\frac{1}{2}}$	49, 439. 87	
$s^2p^4.6p$	^3P	$^2P^o_{1\frac{1}{2}}$	46, 783. 77	
				−1, 697. 54
$s^2p^4.6p$		$^2P^o_{0\frac{1}{2}}$	48, 481. 31	
$s^2p^4.6p$	^3P	$^2S^o_{0\frac{1}{2}}$	47, 847. 30	
$s^2p^4.7s$	^3P	$^2P_{\frac{1}{2}}$	(?)	
$s^2p^4.7s$		$^2P_{1\frac{1}{2}}$	(?)	
$s^2p^4.7s$	^3P	$^4P_{2\frac{1}{2}}$	38, 549. 89	670. 67
$s^2p^4.7s$		$^4P_{1\frac{1}{2}}$	37, 879. 22	
				1, 973. 95
$s^2p^4.7s$		$^4P_{0\frac{1}{2}}$	35, 905. 27	
$s^2p^4.6s$	^1S	$^2S_{0\frac{1}{2}}$	35, 997. 99	

TABLE 4.—*Xenon II, term combinations*

		$(6s)^4P_{3½}$ 78,000.00	$(6s)^4P_{1½}$ 76,004.17	$(6s)^4P_{½}$ 74,210.39	$(6s)^2P_{1½}$ 68,269.62	$(6s)^2P_{½}$ 66,823.18	$(6s)^2D_{2½}$ 64,166.28	$(6s)^2D_{1½}$ 64,162.60	$(5d)X_{1½}$ 67,104.71	$(5d)X_{½}$ 64,788.31
$(s^2p^5)^2P^o_{1½}$	171,067	1,074.50 (15) 93,066	1,051.93 (10) 95,063	1,032.51 (8) 96,851	972.73 (15) 102,803	959.22 (6) 104,251	935.30 (6) 106,917	935.30 (6) 106,917	{961.88} {103,963}	{940.92} {106,279}
$(s^2P^5)^2P^o_{½}$	160,527		1,183.14 (5) 84,520	1,158.48 (7) 86,320	1,083.89 (4) 92,260	1,067.10 (5) 93,712		1,037.71 (8) 96,366	{1,070.4} {93,423}	{1,044.5} {95,739}
$(6p)^4S^o_{1½}$	59,276.51	5,339.37 (150) 18,723.61	5,976.47 (100) 16,727.66	6,694.35 (25) 14,933.85						
$(6p)^4P^o_{2½}$	59,109.67	5,292.22 (300) 18,890.42	5,917.45 (8) 16,894.50							
$(6p)^4P^o_{1½}$	57,556.29	4,890.10 (50) 20,443.79	5,419.17 (200) 18,447.90	{6,002.87} {16,654.10}						
$(6p)^4P^o_{½}$	57,395.74		5,372.41 (100) 18,608.46	5,945.54 (40) 16,814.68						
$(6p)^4D^o_{3½}$	57,363.42	4,844.37 (400) 20,636.77								
$(6p)^4D^o_{2½}$										
$(6p)^4D^o_{1½}$	54,285.52	4,215.63 (70) 23,714.59	4,603.05 (300) 21,718.66	5,017.34 (1–) 19,925.33	7,148.99 (4) 13,984.14	{7,973.8} {12,537.66}				
$(6p)^4D^o_{½}$	50,653.67		3,943.57 (12) 25,350.58	4,243.88 (8) 23,556.73	5,675.15 (1) 17,615.80	{6,182.77} {16,169.51}		{7,400.5} {13,508.93}	6,077.19 (1–) 16,450.43	{7,072.87} {14,134.64}
$(6p)^2D^o_{1½}$	49,439.87	3,500.37 (3) 28,560.27	3,763.38 (4) 26,564.27	4,035.82 (1–) 24,771.14	5,309.28 (40) 18,829.72	5,751.05 (50) 17,383.32	6,788.60 (15) 14,726.52	6,790.34 (9) 14,722.75	5,659.40 (25) 17,664.83	6,115.08 (6) 16,348.50
$(6p)^2D^o_{2½}$	49,012.37	{3,448.76} {28,987.63}	{3,703.78} {26,991.80}		5,191.38 (60) 19,257.35		6,597.24 (40) 15,153.68	6,598.80 (7) 15,150.09	5,525.56 (10) 18,092.70	
$(6p)^2P^o_{½}$	48,481.31		{3,632.31} {27,522.86}	3,885.43 (5) 25,729.91	{5,052.09} {19,788.31}	5,450.49 (25) 18,341.89		6,375.28 (20) 15,681.26	5,368.07 (20) 18,623.50	5,776.40 (25) 17,307.03
$(6p)^2P^o_{1½}$	46,783.77	3,202.56 (1–) 31,216.03	{3,421.29} {29,220.40}	{3,645.06} {27,426.62}	4,653.00 (15) 21,485.51	4,988.78 (20) 20,039.41	5,751.05 (50) 17,383.32	5,752.54 (3) 17,378.82	4,919.68 (20) 20,320.87	5,260.44 (60) 19,004.54
$(6p)^2S^o_{½}$	47,847.30		{3,550.52} {28,156.87}	{3,792.11} {26,363.09}	4,895.24 (1) 20,422.32	5,268.31 (10) 18,976.15		6,127.44 (1) 16,315.52	5,191.38 (60) 19,257.35	5,572.21 (20) 17,941.23

TABLE 4.—*Xenon II, term combinations*—Continued

		$(5p^6)^2S_{\frac{1}{2}}$ 80,194.77	$(5d)^4D_{3\frac{1}{2}}$ 75,630.93	$(5d)^4D_{2\frac{1}{2}}$ 75,671.93	$(5d)^4D_{1\frac{1}{2}}$ 75,035.09	$(5d)^4D_{\frac{1}{2}}$ 75,415.91	$(7s)^4P_{2\frac{1}{2}}$ 38,549.89	$(7s)^4P_{1\frac{1}{2}}$ 37,879.22	$(7s)^4P_{\frac{1}{2}}$ 35,905.27	$(6s)^2S_{\frac{1}{2}}$ 35,997.99
$(5^2p^5)^2P^o_{0\frac{1}{2}}$	171,067	1,100.46 (15) 90,871		1,048.18 (10) 95,403	1,041.30 (12) 96,034	{1,045.5} {95,651}	{754.6} {132,517}	750.76 (4) 133,198	{739.85} {135,162}	740.37 (6) 135,068
$(5^2p^5)^2P^o_{1\frac{1}{2}}$	160,527	1,244.78 (8) 80,335			{1,169.7} {85,492}	{1,174.9} {85,111}		{815.34} {122,648}	{802.43} {124,622}	803.01 (8) 124,531
$(6p)^4S^o_{0\frac{1}{2}}$	59,276.51	4,779.18 (25) 20,918.26		6,097.60 (80) 16,395.37	6,343.97 (50) 15,758.65	6,194.07 (20) 16,140.02	4,823.38 (60) 20,726.57	4,672.17 (20) 21,397.36	{4,277.56} {23,371.24}	{4,294.60} {23,278.52}
$(6p)^4P^o_{0\frac{1}{2}}$	59,109.67		6,051.18(100) 16,521.14	6,036.20 (50) 16,562.14	6,277.54 (30) 15,925.41		4,862.50 (90) 20,559.83	4,708.88 (4) 21,230.55		
$(6p)^4P^o_{1\frac{1}{2}}$	57,556.29	4,416.03 (30) 22,638.43		5,518.69 (1) 18,115.22	5,719.62 (50) 17,478.84	{5,597.67} {17,859.62}	5,259.90 (3) 19,006.49	5,080.66 (80) 19,677.01	4,617.47 (25) 21,650.84	{4,637.29} {21,558.30}
$(6p)^4P^o_{2\frac{1}{2}}$	57,395.74	4,384.92 (20) 22,799.05			5,667.58 (60) 17,639.33	{5,547.80} {18,020.17}		5,122.44 (30) 19,516.52	4,651.96 (50) 21,490.32	4,672.17 (20) 21,397.36
$(6p)^4D^o_{0\frac{1}{2}}$	57,363.42		5,472.62 (70) 18,267.72	5,460.40 (50) 18,308.60			5,313.89 (100) 18,813.39			
$(6p)^4D^o_{1\frac{1}{2}}$										
$(6p)^4D^o_{2\frac{1}{2}}$	54,285.52	3,858.53 (7) 25,909.29		4,674.55 (20) 21,386.47	4,818.04 (50) 20,749.55	4,731.20 (20) 21,130.39	6,353.24 (10) 15,735.66	6,093.53 (25) 16,406.32	5,438.98 (80) 18,380.70	{5,466.69} {18,287.53}
$(6p)^4D^o_{3\frac{1}{2}}$	50,653.67	3,384.13 (4) 29,541.24			4,100.34 (6) 24,381.37	4,037.29 (50) 24,762.12		{7,825.98} {12,774.45}	{6,778.53} {14,748.40}	{6,821.41} {14,655.68}
$(6p)^2D^o_{1\frac{1}{2}}$	49,439.87	3,250.57 (4) 30,755.00		3,811.06 (10) 26,232.00	3,905.89 (3) 25,595.14	3,848.60 (3) 25,976.13	{9,181.1} {10,889.98}	{8,647.7} {11,560.65}	{7,386.4} {13,534.60}	{7,437.4} {13,441.88}
$(6p)^2D^o_{2\frac{1}{2}}$	49,012.37		{3,755.71} {26,618.56}	{3,749.94} {26,659.56}	{3,841.71} {26,022.72}					
$(6p)^2P^o_{0\frac{1}{2}}$	48,481.31	{3,152.32} {31,713.46}			{3,764.87} {26,553.78}	3,711.66 (6) 26,934.48			{7,949.5} {12,576.04}	8,008.49 (20H) 12,483.32
$(6p)^2P^o_{1\frac{1}{2}}$	46,783.77	{2,992.16} {33,411.00}		{3,460.64} {28,888.16}	{3,538.65} {28,251.32}	{3,491.58} {28,632.14}				{9,268.9} {10,785.78}
$(6p)^2S^o_{0\frac{1}{2}}$	47,847.30	{3,090.53} {32,347.47}			{3,677.08} {27,187.79}	{3,626.29} {27,568.61}				{8,437.0} {11,849.31}

The identification of the lines which belong to the Xe_{II} spectrum, as distinguished from those arising from higher stages of ionization, which appear along with the first spark lines in the discharge of a Geissler tube placed in a circuit containing condensers and a spark gap, was effected in two ways. The first was the comparison of spectrograms made with and without inductance in the secondary circuit. The introduction of inductance has the effect of weakening or entirely suppressing lines arising from second and higher stages of ionization. On the other hand, first spark lines remain unchanged or may even be enhanced. The second source of information was the investigation of the spark spectra of argon, krypton, and xenon by L. Bloch, E. Bloch, and Déjardin.[13] From a study of the behavior of the lines in the electrodeless discharge, these observers have assigned each line appearing in their list either to the arc spectrum or to one of the first three ionization stages. The indentifications of all our classified lines which appear in the description by Bloch, Bloch, and Déjardin are in agreement with those which they have published.

Reference should be made to an analysis of the second spectrum of xenon, included in a discussion of the spectra of monatomic gases, published by Hicks [14] in 1919. There is no correspondence between this analysis of Hicks and the one here proposed.

Washington, November 25, 1930.

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[13] L. Bloch, E. Bloch, and Déjardin, Ann. de Phys. (10), 2, p. 461; 1924.
[14] Hicks, Phil. Trans., A 220, p. 335; 1919.

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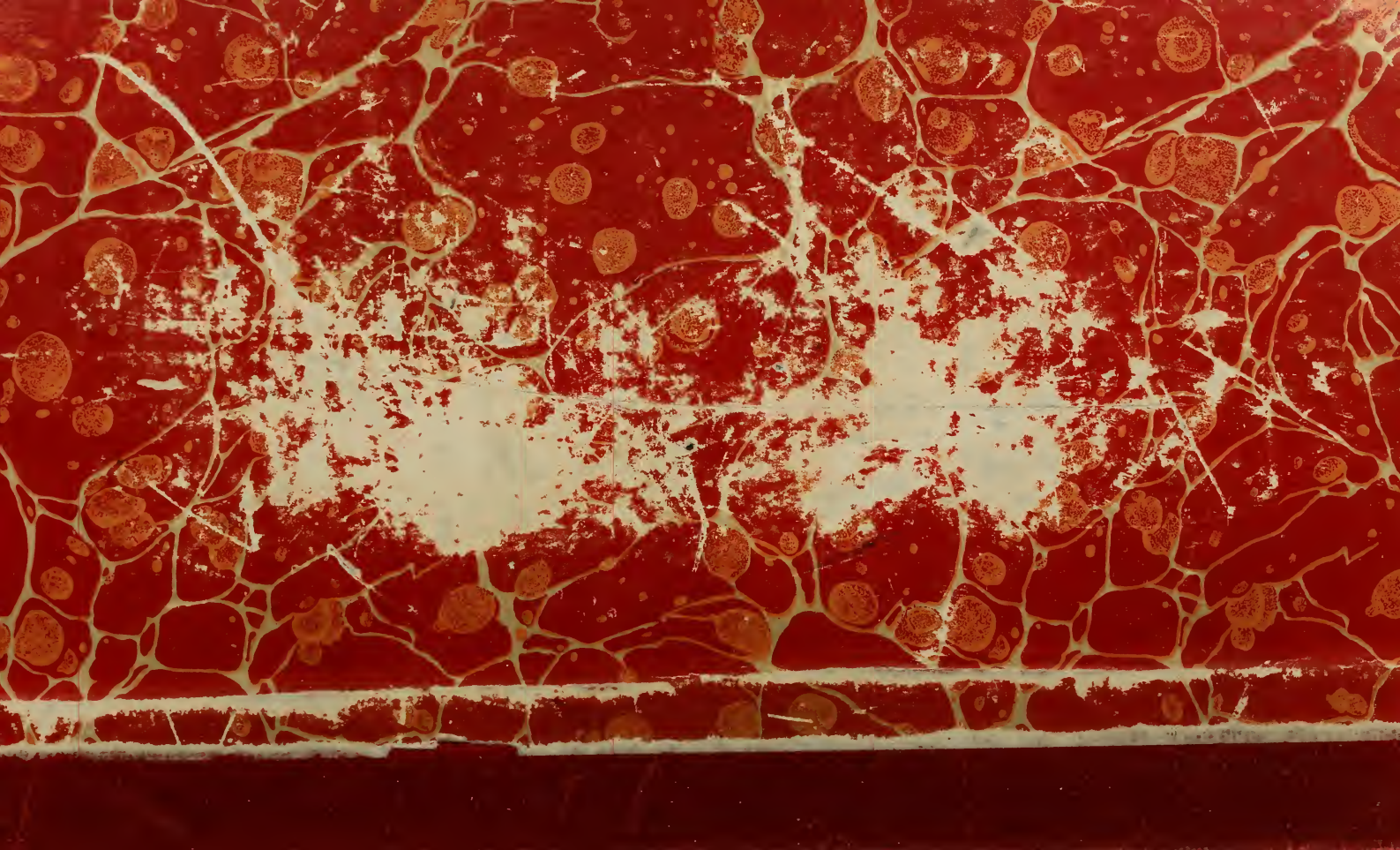
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